

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 118 885 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

25.07.2001 Bulletin 2001/30

(51) Int Cl.7: **G02B 5/30**(21) Application number: **00948326.4**

(86) International application number:

PCT/JP00/05118(22) Date of filing: **28.07.2000**

(87) International publication number:

WO 01/09649 (08.02.2001 Gazette 2001/06)

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(72) Inventors:

- **UCHIYAMA, Akihiko**
Hino-shi Tokyo 191-0065 (JP)
- **KUSHIDA, Takashi**
Hino-shi, Tokyo 191-0065 (JP)

(30) Priority: **29.07.1999 JP 21493999**(74) Representative: **Hallybone, Huw George et al**
CARPMAELS AND RANSFORD
 43 Bloomsbury Square
 London WC1A 2RA (GB)

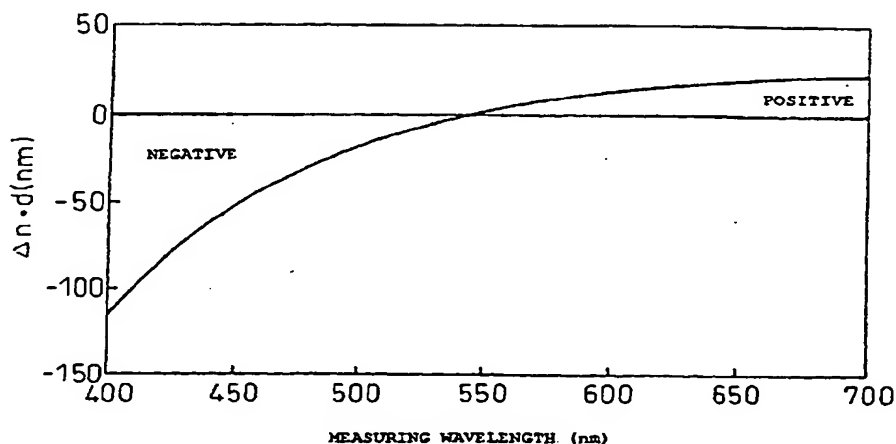
 (71) Applicant: **TEIJIN LIMITED**
 Osaka-shi Osaka 541-0054 (JP)

 (54) **PHASE DIFFERENCE FILM, PHASE DIFFERENCE FILM COMPOSITE AND LIQUID CRYSTAL
DISPLAY DEVICE USING THE SAME**

(57) A retardation film that can compensate for the optical properties of the liquid crystal cells of a liquid crystal display device and thereby enhance image quality. The retardation film consists of a single polymer film, which has a wavelength range in which the retardation value is positive and a wavelength range in which it is negative in a wavelength range of 400-800 nm, and which satisfies the following inequality (1) and/or (2) and has a water absorption of no greater than 1% by mass.

$$|R(400)| \geq 10 \text{ nm} \quad (1)$$

$$|R(700)| \geq 10 \text{ nm} \quad (2)$$

Fig. 5

EP 1 118 885 A1

BEST AVAILABLE COPY

Printed by Jouve, 75001 PARIS (FR)

[0010] It is yet another object of the invention to provide a novel laminated retardation film or retardation film-integrated polarizing film with improved optical qualities over other retardation films or polarizing films by combination with the aforementioned retardation film.

[0011] It is yet another object of the invention to provide a retardation film that is useful for optical apparatuses such as liquid crystal display devices.

Disclosure of the Invention

[0012] The present inventors have studied a wide variety of materials with excellent optical properties, but for the optical uses of retardation films, attention was focused on polymer materials as transparent materials with low light absorption at the measuring wavelength, materials with a glass transition temperature of 100°C or higher, preferably 120°C or higher and especially 150°C or higher, and materials that exhibit favorable molding properties. Polymer materials may be crystalline, amorphous, or liquid crystalline, but amorphous polymers usually allow solvent casting process and are therefore preferred for purposes in which retardation irregularities and the like must be minimized, such as with retardation films. From this standpoint, polycarbonates, polyesters, polyallylates, polyolefins and the like are best as polymer materials, but it is believed that polycarbonates are particularly advantageous from the viewpoint of productivity and increasing freedom of molecular design for copolymerization and the like.

[0013] The present inventors also researched the optical properties, and found that a polymer film with excellent properties as a retardation film can be obtained by stretching a polymer film composed of a polymer blend comprising a polymer with positive refractive index anisotropy and a polymer with negative refractive index anisotropy, a copolymer made from a monomer component of a polymer with positive refractive index anisotropy and a monomer component of a polymer with negative refractive index anisotropy, or a combination thereof. The polymers with positive and negative refractive index anisotropy referred to here are defined as follows: a polymer with positive refractive index anisotropy is one wherein the direction of the maximum refractive index in the in-plane direction of the film, i.e. the slow axis, matches the stretching direction when the polymer film is uniaxially stretched, and a polymer with negative refractive index anisotropy is one wherein the slow axis is roughly perpendicular to the stretching direction. Some materials, like polystyrene, have positive refractive index anisotropy or negative refractive index anisotropy depending on the conditions of uniaxial stretching, but here it is defined as the refractive index anisotropy exhibited upon uniaxial stretching from 10°C below the glass transition temperature to 20°C above the glass transition temperature, as the usual stretching temperature conditions for fabrication of a commercially available retardation film. These measurements are made by polarized light analysis at a wavelength of 550 nm.

[0014] Retardation films characterized by having a range in which the retardation value is positive and a range in which it is negative in a measuring wavelength range of from 400 to 800 nm with a single retardation film are unknown to the prior art. The present inventors have conducted diligent research on materials that give such retardation films, and have completed the present invention upon the discovery that polymers such as certain polycarbonates and blends of polyphenylene oxide and polystyrene are effective to this purpose, and that such retardation films can be fabricated by appropriate selection of the polymers.

[0015] It was further found that such retardation films can be used as laminates with other retardation films to control the retardation wavelength dispersion of the other retardation films and thus contribute to enhanced image quality for liquid crystal display devices.

[0016] In other words, the present invention is accomplished by a retardation film consisting of a single polymer film, which has a wavelength range in which the retardation value is positive and a wavelength range in which it is negative in a wavelength range of 400-800 nm, which satisfies the following inequality (1) and/or (2), and which has a water absorption of no greater than 1% by mass.

$$|R(400)| \geq 10 \text{ nm} \quad (1)$$

$$|R(700)| \geq 10 \text{ nm} \quad (2)$$

where $|R(400)|$ and $|R(700)|$ represent the retardation values at wavelengths of 400 nm and 700 nm, respectively.

[0017] The retardation film of the invention is believed to be based on the following principle. That is, presumably, when the retardation value of the component with positive refractive index anisotropy and the retardation value of the component with negative refractive index anisotropy completely cancel each other out, the retardation value is exactly zero. However, because the polymer has wavelength dispersion in its birefringence, appropriate adjustment of the amount of the component with the positive refractive index anisotropy and the amount of the component with the negative refractive index anisotropy produces a phenomenon such that the retardation value is exactly zero at a wave-

and preferably no greater than 0.5% by mass. (Polymer film material)

[0029] The polymer material used for the retardation film of the invention is not particularly restricted and may be any blend or copolymer or their combination that satisfies the aforementioned conditions, although preferred are materials with excellent heat resistance, satisfactory optical performance and suitability to solution film formation, with thermoplastic polymers being especially preferred. For example, one or more types may be appropriately selected from among polyacrylates, polyesters, polycarbonates, polyolefins, polyethers, polysulfon-based copolymers, polysulfone, polyethersulfone and the like. However, in terms of the practicality of the retardation film, the water absorption of the polymer film is limited to no greater than 1% by weight.

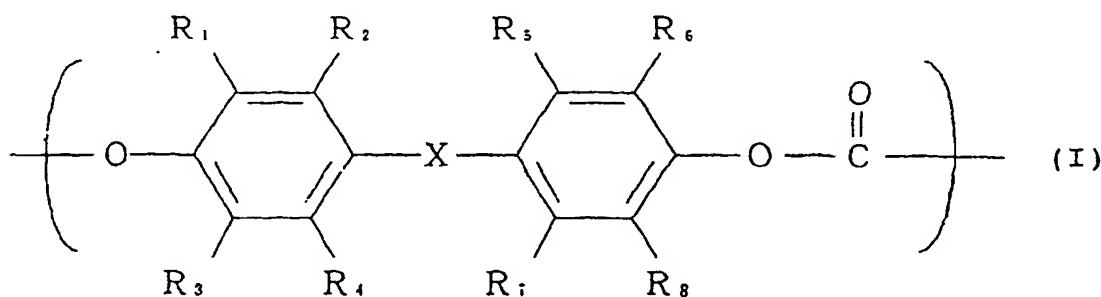
[0030] A blend polymer must be optically transparent, and therefore it is preferably a compatible blend or one that has roughly equal refractive indexes for each polymer. As suitable examples of specific combinations of blend polymers there may be mentioned combinations of polymers having negative optical anisotropy such as poly(methyl methacrylate) with polymers having positive optical anisotropy such as poly(vinylidene fluoride), poly(ethylene oxide) and poly(vinylidene fluoride-co-trifluoroethylene), combinations of polymers having positive optical anisotropy such as poly(phenylene oxide) with polymers having negative optical anisotropy such as polystyrene, poly(styrene-co-lauroyl maleimide), poly(styrene-co-cyclohexyl maleimide) and poly(styrene-co-phenyl maleimide), a combination of poly(styrene-co-maleic anhydride) having negative optical anisotropy with polycarbonate having positive optical anisotropy, and a combination of poly(acrylonitrile-co-butadiene) having positive optical anisotropy with poly(acrylonitrile-co-styrene) having negative optical anisotropy; however, there is no limitation to these. From the standpoint of transparency, a combination of polystyrene with a poly(phenylene oxide) such as poly(2,6-dimethyl-1,4-phenylene oxide) is particularly preferred. For such combinations, the proportion of the polystyrene preferably constitutes from 61% by mass to 75% by mass of the whole.

[0031] Examples of copolymers that may be used include poly(butadiene-co-styrene), poly(ethylene-co-styrene), poly(acrylonitrile-co-butadiene), poly(acrylonitrile-co-butadiene-co-styrene), polycarbonate copolymers, polyester copolymers, polyester carbonate copolymers and polyallylate copolymers. Polycarbonate copolymers, polyester copolymers, polyester carbonate copolymers, polyallylate copolymers and the like that have fluorene skeletons are particularly preferred because the fluorene skeleton segments can provide negative optical anisotropy.

(Polycarbonate films with fluorene skeleton)

[0032] Particularly preferred for use as the polymer film for the retardation film of the invention are polycarbonate copolymers produced by reaction of a bisphenol with phosgene or a compound that forms a carbonic acid ester such as diphenyl carbonate, because of their excellent transparency, heat resistance and productivity. Preferred polycarbonate copolymers are copolymers containing structures with fluorene skeletons. The component with the fluorene skeleton is preferably included at 1-99 mole percent.

[0033] Suitable polycarbonates for the polymer film of the retardation film of the invention are materials that give a polymer film of a polycarbonate composed of a repeating unit represented by the following formula (I):



where R_1 - R_8 are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms, and X is

and $-R_{23}-$,

where R_{17} - R_{19} , R_{21} and R_{22} in Y are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-22 carbon atoms, R_{20} and R_{23} are each independently selected from among hydrocarbon groups of 1-20 carbon atoms, and Ar is selected from among aryl groups of 6-10 carbon atoms,

such that the repeating unit represented by formula (I) constitutes 30-90 mole percent of the total polycarbonate and the repeating unit represented by formula (II) constitutes 70-10 mole percent of the whole.

[0034] The material is a polycarbonate copolymer consisting of a repeating unit with a fluorene skeleton represented by formula (I) above and a repeating unit represented by formula (II) above, or a composition containing a polycarbonate comprising a repeating unit with a fluorene skeleton represented by formula (I) above and a polycarbonate comprising a repeating unit represented by formula (II) above (hereunder also referred to as "blend polymer"). In the case of a copolymer, two or more of each of the repeating units represented by formulas (I) and (II) may be combined, and in the case of a composition as well, two or more of the aforementioned repeating units may be used in combination.

[0035] In formula (I), R_1 - R_8 are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms. As hydrocarbon groups of 1-6 carbon atoms there may be mentioned alkyl groups such as methyl, ethyl, isopropyl and cyclohexyl, and aryl groups such as phenyl. Of these, hydrogen and methyl are preferred.

[0036] In formula (II), R_9 - R_{16} are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-22 carbon atoms. As hydrocarbon groups of 1-22 carbon atoms there may be mentioned alkyl groups of 1-9 carbon atoms such as methyl, ethyl, isopropyl and cyclohexyl, and aryl groups such as phenyl, biphenyl and terphenyl. Of these, hydrogen and methyl are preferred.

[0037] In Y of formula (II), R_{17} - R_{19} , R_{21} and R_{22} are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-22 carbon atoms, which hydrocarbon groups may be the same as those mentioned above. R_{20} and R_{23} are selected from among hydrocarbon groups of 1-20 carbon atoms, which hydrocarbon groups may also be the same as those mentioned above. Ar is selected from among aryl groups of 6-10 carbon atoms such as phenyl and naphthyl.

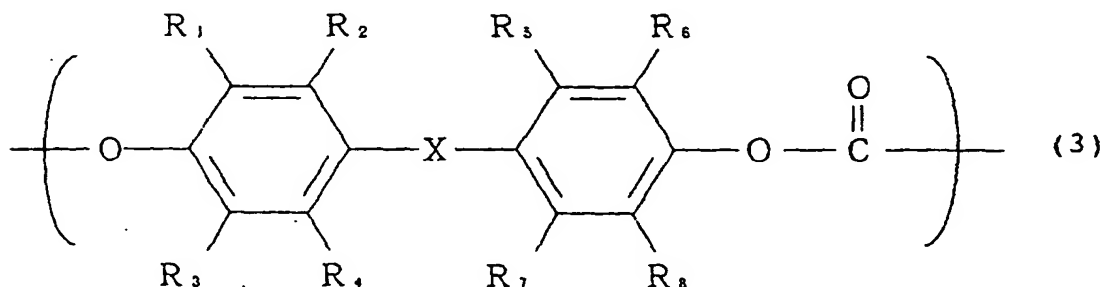
[0038] The content of formula (I), i.e. the copolymer composition ratio in the case of a copolymer or the blend composition ratio in the case of a composition, is 30-90 mole percent of the total polycarbonate. Outside of this range, the film will not have a wavelength range in which the retardation value is positive and a wavelength range in which it is negative for a measuring wavelength of 400-800 nm, using a single retardation film. The content of formula (I) is preferably 35-85 mole percent, and more preferably 40-80 mole percent, of the total polycarbonate.

[0039] Here, the molar ratio can be determined by, for example, nuclear magnetic resonance (NMR) with the total bulk of the polycarbonate composing the polymer film, whether in the case of a copolymer or a blend polymer.

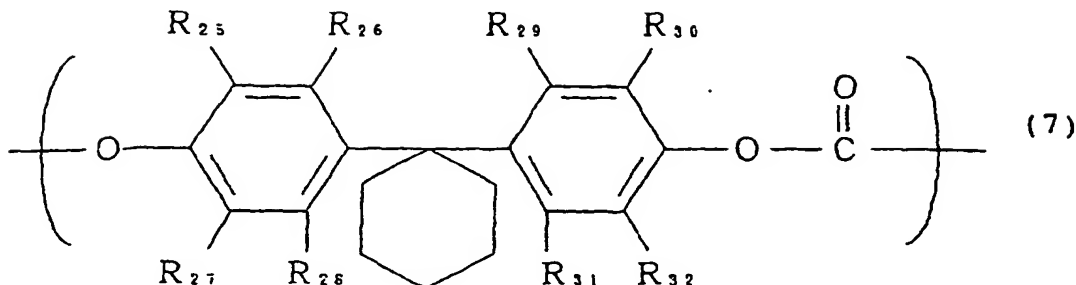
[0040] The aforementioned copolymers and/or blend polymers can be produced by publicly known processes. For polycarbonates, polycondensation processes and melt polycondensation processes with dihydroxy compounds and phosgene may be suitably used. For blends, compatible blends are preferred but even if they are not totally compatible the refractive indexes of the components can be matched to minimize light scattering between the components and improve the transparency.

[0041] Of the aforementioned polycarbonates with fluorene skeletons, the following first, second and third copolymer polycarbonate types are particularly suitable as materials for the polymer film composing the retardation film of the invention.

[0042] First polycarbonate type: Polycarbonates composed of a repeating unit represented by the following formula (3):



where R_1 - R_8 are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms, and X is the following formula (4)



where R_{25} - R_{32} are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms,

such that the repeating unit represented by formula (1) constitutes 55-85 mole percent of the total polycarbonate and the repeating unit represented by formula (7) constitutes 45-15 mole percent thereof.

[0045] For the first, second and third polycarbonates, in formula (3), R_1 - R_8 are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms. As examples of hydrocarbon groups of 1-6 carbon atoms there may be mentioned methyl, ethyl, propyl, butyl and the like. X is a fluorene ring. Preferably, R_1 - R_8 are all hydrogen, or else either or both R_1 and R_3 are methyl and either or both R_6 and R_8 are methyl group.

[0046] For the first polycarbonate, in the repeating unit represented by formula (5) above; R_9 - R_{16} are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms. As hydrocarbon groups of 1-6 carbon atoms there may be mentioned methyl, ethyl, propyl, butyl and the like. In formula (5), R_9 - R_{16} are preferably hydrogen atoms.

[0047] The repeating unit represented by formula (3) constitutes 60-90 mole percent of the total polycarbonate and the repeating unit represented by formula (5) constitutes 40-10 mole percent thereof. Outside of these ranges, the film will not have both positive and negative retardation value ranges at wavelengths from 400-800 nm. Although it will depend on the conditions, when the film is fabricated under ordinary uniaxial stretching conditions such as those employed in the examples described below, the single polycarbonate film can serve as a retardation film with a negative retardation value at a wavelength of 400 nm and a positive retardation value at 800 nm, thus having a wavelength range in which the retardation is positive and a wavelength range in which it is negative within that region, by including the repeating unit represented by formula (3) at 71-79 mole percent of the total polycarbonate and including the repeating unit represented by formula (5) at 29-21 mole percent thereof.

[0048] For the second polycarbonate, in the repeating unit represented by formula (6), R_{17} - R_{24} are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms. As examples of hydrocarbon groups of 1-6 carbon atoms there may be mentioned methyl, ethyl, propyl, butyl and the like. In formula (6), R_{17} - R_{24} are preferably hydrogen atoms.

[0049] The repeating unit represented by formula (3) constitutes 55-85 mole percent of the total polycarbonate and the repeating unit represented by formula (6) constitutes 45-15 mole percent thereof. Outside of these ranges, the film will not have both positive and negative retardation value ranges at wavelengths from 400-800 nm. Although it will depend on the conditions, when the film is fabricated under ordinary uniaxial stretching conditions such as those employed in the examples described below, the single polycarbonate film can serve as a retardation film with a negative retardation value at a wavelength of 400 nm and a positive retardation value at 800 nm, thus having a wavelength range in which the retardation is positive and a wavelength range in which it is negative within that region, by including the repeating unit represented by formula (3) at 65-73 mole percent of the total polycarbonate and including the repeating unit represented by formula (6) at 35-27 mole percent thereof.

[0050] For the third polycarbonate, in the repeating unit represented by formula (7), R_{25} - R_{32} are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms. As examples of hydrocarbon groups of 1-6 carbon atoms there may be mentioned methyl, ethyl, propyl, butyl and the like. In formula (7), R_{25} - R_{32} are preferably hydrogen atoms.

[0051] The repeating unit represented by formula (3) constitutes 55-85 mole percent of the total polycarbonate and the repeating unit represented by formula (7) constitutes 45-15 mole percent thereof. Outside of these ranges, the film will not have both positive and negative retardation value ranges at wavelengths from 400-800 nm. Although it will depend on the conditions, when the film is fabricated under ordinary uniaxial stretching conditions such as those employed in the examples described below, the single polycarbonate film can serve as a retardation film with a negative retardation value at a wavelength of 400 nm and a positive retardation value at 800 nm, thus having a wavelength range in which the retardation is positive and a wavelength range in which it is negative within that region, by including the repeating unit represented by formula (3) at 66-74 mole percent of the total polycarbonate and including the re-

(Addition of low molecular compound with optical anisotropy)

[0067] A low molecular compound with optical anisotropy may be added to the retardation film made of a polymer material according to the invention, so long as it has a wavelength range in which the retardation value is positive and a wavelength range in which it is negative, in a wavelength range of 400-800 nm. In such cases, the amount of the low molecular compound is preferably no greater than 20 parts by mass and preferably no greater than 10 parts by mass, to 100 parts by mass of the total retardation film. The purpose of adding a low molecular compound is to achieve delicate control of the retardation wavelength dispersion, but if it exceeds 20 parts by mass it may notably lower the glass transition temperature of the polymer material, or precipitate from the polymer material, or in some cases, it may cause phase separation and produce turbidity, thus making it impossible to maintain transparency. The retardation film of the invention is composed substantially of a polymer material and its properties are utilized to realize a unique wavelength dispersion of retardation; the low molecular compound serves only as an additive to complement the properties of the polymer. Because the retardation film of the invention is made essentially by stretching at near the glass transition temperature of the polymer material, the low molecular compound is preferably one that does not sublime or gasify at the glass transition temperature of the polymer material to which it is added. The low molecular compound is also preferably one with good compatibility with the polymer material of the retardation film, or if it has poor compatibility, one which has a matching refractive index so that transparency is not lost.

[0068] The low molecular compound with optical anisotropy mentioned here is a compound which has an asymmetrical molecular structure for anisotropy of the refractive index of the molecular structure, and it is preferably organic with a molecular weight of no greater than 3000. Whether or not a low molecular compound has optical anisotropy is determined by whether or not the retardation wavelength dispersion of the retardation film changes between when it is added and when it is not added to a retardation film of the invention. That is, a low molecular compound with optical anisotropy as defined here is one which, when added to a retardation film, changes the retardation wavelength dispersion of the retardation film. As mentioned above, the molecular weight is preferably not over 3000, since this will tend to result in phase separation with the polymer material, which is the primary material of the retardation film.

[0069] While there are no particular restrictions on such low molecular compounds, there may be mentioned as examples, liquid crystals, polymerizable liquid crystals, saccharose acetate, xylene, toluene, biphenyl, terphenyl, dichromatic colorants, colorants, dyes, pigments, near infrared absorbing colorants, oligomers, dialkyl phthalates, and the like.

[0070] The method of addition may be any publicly known method commonly used for addition of polymer material plasticizers or the like. The aforementioned low molecular compound may also serve as a plasticizer.

[0071] When a polycarbonate such as mentioned above is used as the polymer film of the invention, addition of the low molecular compound with refractive index anisotropy may result in a slight shift in the preferred copolymerization ratio (molar ratio) of the polycarbonate.

(Other additives)

[0072] There may also be added to the retardation film of the invention various ultraviolet absorbers such as phenylsalicylic acid, 2-hydroxybenzophenone and triphenylphosphate, or bluing agents for adjustment of the color, antioxidants, and the like.

(Film thickness)

[0073] The thickness of the retardation film is preferably from 1 μm to 400 μm . It is more preferably 10-200 μm , and even more preferably 30-150 μm .

(Modification of other optical properties of the film)

[0074] One of the properties sometimes required for a retardation film used for a liquid crystal display device or reflective polarizing film is the requirement that the retardation not change even when the angle of incidence to the retardation film changes from normal incidence to oblique incidence. In such cases, the value of $N_z(n_x - n_z)/(n_x - n_y)$, expressed in terms of the three-dimensional refractive index n_x , n_y and n_z , is preferably between 0.3 and 1.5. In particular, when $N_z = 0.5$, there is virtually no change in the retardation even when the angle of incidence to the retardation film changes from normal incidence to oblique incidence. The three-dimensional refractive index is obtained by measuring the incident angle dependence of retardation, assuming the retardation film as a refractive index spheroid. The measuring wavelength is established at 400-800 nm, and preferably 400-780 nm, but it may also be established at 400-700 nm.

[0075] By appropriate use of publicly known stretching techniques and film forming techniques for the polymer film

[0083] In such cases, since both are laminated with their stretching axes parallel, if both of the films have been fabricated by longitudinal uniaxial stretching, for example, it is possible to carry out the attachment step in a roll-to-roll manner, which is highly advantageous from the standpoint of productivity. When fabricating a wide-band $\lambda/4$ film with such a combination, a film with a smaller retardation at shorter wavelengths may be used for retardation wavelength dispersion of a retardation film with a positive retardation value, for example.

[0084] These will be explained in further detail by means of Examples, but it is possible to control the wavelength dispersion property of the retardation by laminating the retardation films in this manner.

[0085] Incidentally, while some control of the retardation is possible even by the method of Japanese Patent Publication No. 2609139, it requires a plurality of positive or negative films. On the other hand, a retardation film according to the invention which has retardation wavelength dispersion such that the retardation is negative at the short wavelength end and positive at the long wavelength end can be laminated with another single retardation film with a certain wavelength dispersion, so that, when it is not desired to change the retardation value of the other retardation film at a measuring wavelength of 550 nm, for example, the retardation wavelength dispersion can be controlled very delicately for retardation which is smaller at the shorter wavelength end than that wavelength and larger at the longer wavelength end. A retardation film characterized by having a range in which the retardation value is positive and a range in which it is negative, at measuring wavelengths of 400-800 nm according to the invention, may not only be used in combination with other retardation films in this manner but, by itself, it can also compensate for optical properties of liquid crystal cells of liquid crystal display devices, and enhance image quality.

[0086] The retardation film of the invention can also be used in combination with a polarizing film or the like in the optical elements not only of liquid crystal display devices but also of other display devices, such as organic electroluminescence displays (also referred to as OLEDs), plasma displays, field emission displays, inorganic electroluminescence displays and the other light emitting elements.

[0087] The material for a retardation film with a positive retardation value in the total wavelength range of 400-800 nm is preferably a polymer material, and examples of preferred ones include polycarbonates, polyesters, polyallylates, polyolefins, polyethers, polyphenylene oxides, polysulfones, polyethersulfones, polyvinyl alcohols, amorphous polyolefins, liquid crystal polymers, polymerizable liquid crystals which have been oriented and hardened, etc. The material for a negative retardation film is preferably polystyrene, polycarbonates with fluorene skeletons, triacetyl cellulose, etc. Polycarbonates are particularly preferred from the standpoint of transparency and high heat resistance and, as examples of bisphenol components composing such polycarbonates, there may be mentioned bisphenol A, bisresol, bisphenols with fluorene skeletons, bisphenols with isophorone skeletons or the like, bisphenols with cyclohexane skeletons, and the like. Copolymers of two or more of these may also be used. More preferred are homopolymers with bisphenol A as the bisphenol component.

[0088] Optical compensating films composed of discotic liquid crystals, polymer liquid crystals with a twisted structure, etc. may also be laminated with the retardation film of the invention.

[0089] When the retardation film of the invention is laminated with another retardation film and used as a quarter-wave film, it is preferred for the retardation value to be $1/4$ wavelength at a measuring wavelength of 550 nm, and more specifically, the retardation value is preferably from 110 nm to 160 nm. This value will be set depending on the purpose of use. This quarter-wave film may be used as an element that converts circularly polarized light to linearly polarized light or linearly polarized light to circularly polarized light in a reflective liquid crystal display device using only one polarizing film or in a reflective liquid crystal display device comprising a combination of guest-host crystals and a quarter-wave film, or as an element that converts circularly polarized light to linearly polarized light, in combination with an element that only reflects circularly polarized light on one side which is used as a brightness-enhancing film of a backlight-equipped transmission liquid crystal display device.

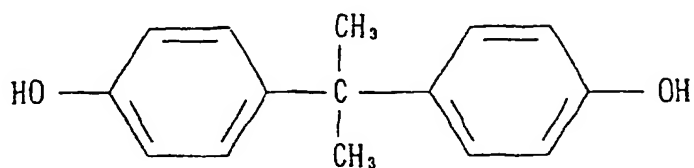
(Retardation film-integrated polarizing film)

[0090] The retardation film of the invention can realize effects that are difficult to achieve with combinations of ordinary retardation films, by preparing a retardation film-integrated polarizing film which is a combination of, for example, an ordinary polarizing film comprising a dichromic absorbing substance such as iodine or a dye, or a reflective polarizing film that reflects or diffuses only polarized light on one side. For example, a retardation film of the invention having a retardation of approximately zero at a measuring wavelength of 550 nm, a negative retardation at shorter wavelengths and a positive retardation at longer wavelengths may be used in combination with a dichromic absorbing polarizing film to avoid changing the linearly polarized state at a measuring wavelength of 550 nm while changing only the polarized state at other wavelengths, thereby allowing a change of the wavelength dispersion of the outgoing polarization state of the polarizing film.

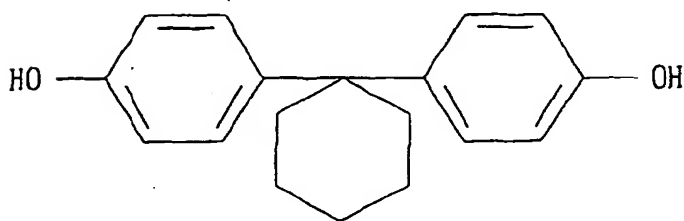
[0091] Also, while triacetyl cellulose films have conventionally been used as protective films for polarizing films containing iodine or dichromic pigments added to polyvinyl alcohol, a retardation film of the invention may be used in place of such a protective film. For improved adhesion with the polarizing film in such a case, various types of coating agents

(5) Polycarbonate monomers

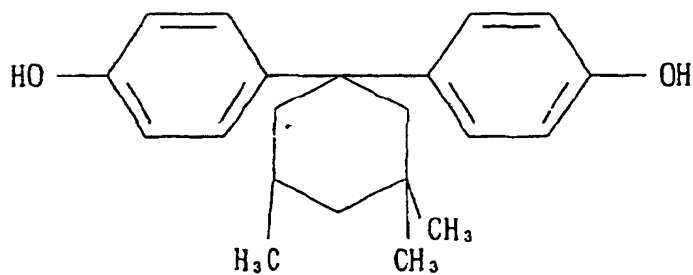
[0102] The structures of the polycarbonate monomers used in the following examples and comparative examples were as follows.



[A]



[B]



[C]

the long wavelength end.

Reference Example 1

[0108] A polycarbonate copolymer was obtained by the same method as Example 1, except that the monomers listed in Table 1 were used. This was used to fabricate a retardation film in the same manner as Example 1 except that the stretching conditions were 160°C and a factor of 1.1. The retardation film had positive refractive index anisotropy and had the retardation dispersion values shown in Table 1.

Example 4

[0109] The retardation film fabricated in Example 1 and the retardation film of Reference Example 1 were attached using an adhesive in such a manner that their stretching axes were parallel. The retardation wavelength dispersion properties of the laminated retardation film are shown in Table 2 and Fig. 6. The laminated retardation film had a larger retardation with longer wavelengths, indicating that the retardation film had retardation of approximately a quarter wavelength in a wide range.

[0110] This laminated retardation film and a commercially available polarizing film ("LLC2-9218", trade name of San-ritsu, KK.) were attached via an adhesive in such a manner that the absorption axis of the polarizing film and the delay axis of the retardation film were arranged at 45°. After removing the touch panel, polarizing film and retardation film on the observer side of the liquid crystal layer of a reflective color liquid crystal display device of a portable data terminal ("Zaurus Color Pocket MI-310", trade name of Sharp Corp.), the retardation film-integrated polarizing film was attached via an adhesive at an appropriate angle. The portable data terminal was activated, and a display device was thus obtained with excellent image quality exhibiting no coloration of the black state.

Reference Example 2

[0111] A polycarbonate copolymer was obtained by the same method as Example 1, except that the monomers listed in Table 1 were used. This was used to fabricate a retardation film in the same manner as Example 1 except that the stretching conditions were 161°C and a factor of 1.2. The retardation film had positive refractive index anisotropy and had the retardation dispersion values shown in Table 1.

Example 5

[0112] The monomers listed in Table 1 were used to fabricate a polycarbonate copolymer in the same manner as Example 1. The sample with a ratio of monomers [A] and [D] of 26:74 (mol%) had negative retardation at the short wavelength end and positive retardation at the long wavelength end. The retardation dispersion values are shown in Table 1.

Example 6

[0113] The retardation film of Example 5 and the retardation film of Reference Example 2 were attached using an adhesive in such a manner that their stretching axes were parallel. The retardation wavelength dispersion properties of the laminated retardation film are shown in Table 2. The laminated retardation film had a smaller retardation with longer wavelengths. The laminated retardation film had a large $\Delta n \cdot d(450)/\Delta n \cdot d(550)$ value of 1.18 and a large liquid crystal cell retardation wavelength dispersion, thus exhibiting satisfactory properties for a high-speed response super twisted nematic liquid crystal display device.

Example 7

[0114] A methylene chloride dope solution with a solid concentration of 20% by mass was prepared using 1.5 parts by mass of saccharose octaacetate to 98.5 parts by mass of the polycarbonate copolymerized in Example 1. A cast film with a thickness of 120 μm was fabricated from the dope solution, and it was uniaxially stretched to a draw factor of 1.2 at a temperature of 240°C to make a retardation film having the retardation wavelength dispersion values shown in Table 1. Table 1 confirms that at measuring wavelengths of 400-800 nm, the retardation wavelength dispersion value is negative at the shorter wavelength end and positive at the longer wavelength end, but a different retardation wavelength dispersion from Example 1 was obtained.

EP 1 118 885 A1

Table 3 (continued)

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
$\Delta n-d$ (550) (nm)	128	-73	129	-64	191	-27
$\Delta n-d$ (650) (nm)	126	-67	126	-60	188	-25

Example 8

[0116] Polystyrene (Catalog No. 18242-7, product of Aldrich Chemical Co.) and poly(2,6-dimethyl-1,4-phenylene oxide) (Catalog No. 18178-1, product of Aldrich Chemical Co.) were dissolved in chloroform at respective proportions of 66.5% by mass and 33.5% by mass, to prepare a dope solution with a solid concentration of 18% by mass. A cast film was fabricated from the dope solution and uniaxially stretched to a factor of 2 at a temperature of 130°C.

[0117] The thickness of the film was 90 μm , the retardation value at a measuring wavelength of 400 nm was 82 nm, the retardation value at a wavelength of 700 nm was -18 nm, and the water absorption was 0.3% by mass. Table 4 shows the retardation values at 3 wavelengths and the values for the retardation wavelength dispersion properties at wavelengths of 450 and 650 nm with respect to the retardation value $R(550\text{ nm})$, or $R(450)/R(550)$, $R(650)/R(550)$. Fig. 7 is a graph showing the retardation wavelength dispersion properties. This film had positive retardation with a measuring wavelength at the shorter wavelength end and a negative retardation at the longer wavelength end.

Example 9

[0118] A polycarbonate with a viscosity-average molecular weight of 38,000 ("Panlite C1400 Grade", trade name of Teijin Chemical Co., Ltd.) obtained by polymerization of bisphenol A and phosgene was dissolved in methylene chloride to prepare a dope solution with a solid concentration of 20% by mass, and this dope was used for solution casting to fabricate a polycarbonate film with a thickness of 100 μm . The film was subjected to longitudinal uniaxial stretching to a factor of 1.1 at 160°C to obtain a retardation plate with a positive retardation value. The properties are shown in Table 4 and Fig. 8. This retardation plate was attached to the retardation plate of Example 8 via an adhesive in such a manner that their stretching directions were perpendicular. The retardation wavelength dispersion properties of the laminated retardation plate are shown in Table 4 and Fig. 8. The laminated retardation plate had a delay axis in the stretching direction of the polycarbonate, and as shown in Fig. 8, the retardation was smaller with shorter measuring wavelength and it functioned as a quarter waveplate in a considerably wide range.

[0119] This retardation plate was attached to a commercially available polarizing plate in such a manner that the polarizing axis thereof was arranged at 45° with the delay axis of the retardation plate, and was then substituted for the polarizing plate and retardation plate on the observer side of a reflective color liquid crystal display device of a commercially available portable data terminal, "Zaurus Color Pocket MI-310™". The result was a liquid crystal display device with excellent image quality.

Example 10

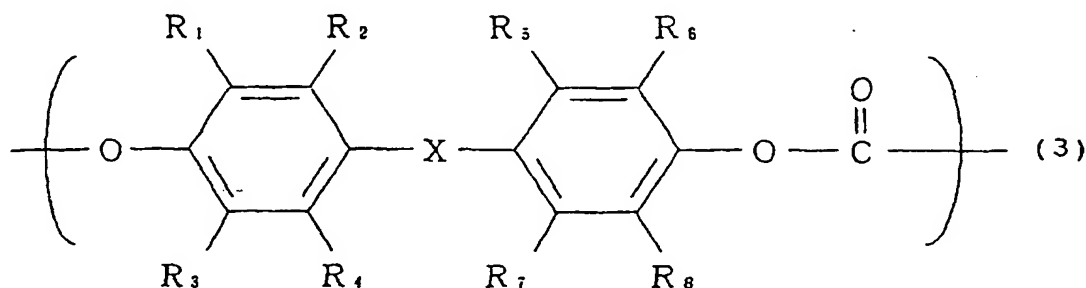
[0120] A polycarbonate with a viscosity-average molecular weight of 38,000 ("Panlite C1400 Grade", trade name of Teijin Chemical Co., Ltd.) obtained by polymerization of bisphenol A and phosgene was dissolved in methylene chloride to prepare a dope solution with a solid concentration of 20% by mass, and this dope was used for solution casting to fabricate a polycarbonate film with a thickness of 100 μm . The film was subjected to longitudinal uniaxial stretching to a factor of 1.2 at 162°C to obtain a retardation plate with a positive retardation value. The properties are shown in Table 4 and Fig. 9. This retardation plate was attached to the retardation plate of Example 8 via an adhesive in such a manner that their stretching directions matched. The retardation wavelength dispersion properties of the laminated retardation plate are shown in Table 4 and Fig. 9. The laminated retardation plate had a delay axis in the stretching direction of the polycarbonate, and while there was virtually no change in the retardation at a measuring wavelength of 550 nm, with shorter wavelengths the retardation was larger than the polycarbonate retardation plate alone.

Comparative Example 7

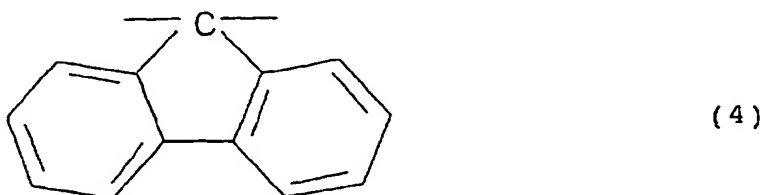
[0121] The polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) used in Example 8 were dissolved in chloroform to respective proportions of 80% by mass and 20% by mass, to prepare a dope solution with a solid concentration of 18% by mass. A cast film was formed from this doping solution, and was subjected to uniaxial stretching to a factor of 1.7 at a temperature of 130°C.

[0122] The retardation wavelength dispersion properties are shown in Table 4. The film was a negative retardation

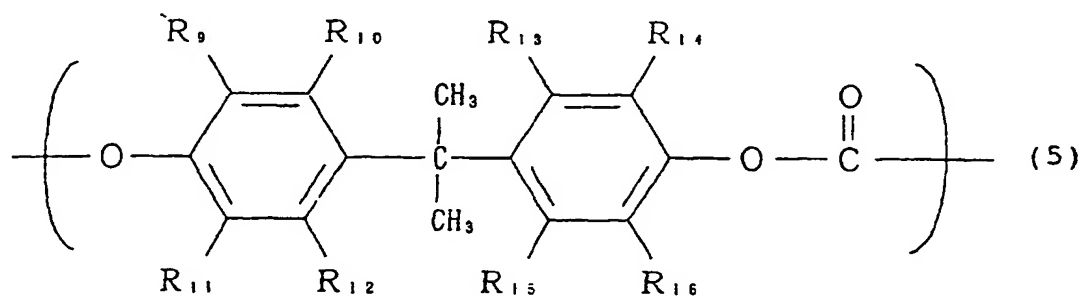
4. A retardation film according to claim 3, wherein said polymer film is a polycarbonate film with a fluorene skeleton.
5. A retardation film according to claim 4, wherein the polymer film comprises a polycarbonate composed of a repeating unit represented by the following formula (3):



where R_1 - R_8 are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms, and X is the following formula (4)



and a repeating unit represented by the following formula (5):



where R_9 - R_{16} are each independently selected from among hydrogen, halogen atoms and hydrocarbon groups of 1-6 carbon atoms,

and the repeating unit represented by formula (3) constitutes 60-90 mole percent of the total polycarbonate and the repeating unit represented by formula (5) constitutes 40-10 mole percent thereof.

6. A retardation film according to claim 1, wherein the retardation value is positive at a wavelength of 400 nm and the retardation value is negative at 800 nm.
7. A retardation film according to claim 1 or 6, wherein the polymer film is a single polymer blend film comprising polyphenylene oxide and polystyrene.
8. A retardation film according to claim 7, wherein the polymer film is a single polymer blend film comprising 39-25% by mass of polyphenylene oxide and 61-75% by mass of polystyrene.
9. A retardation film according to any one of claims 1 to 8, wherein the polymer film further contains up to 20% by

Fig.1

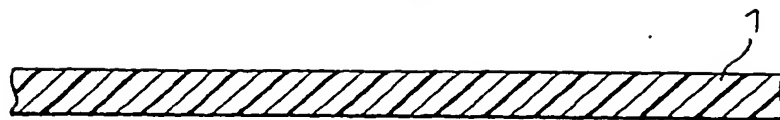


Fig.2

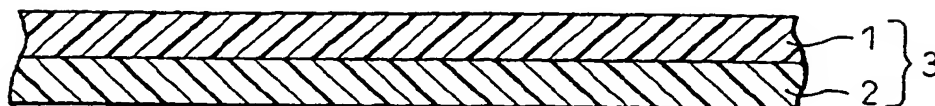


Fig.3

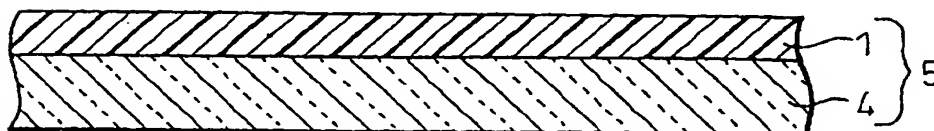
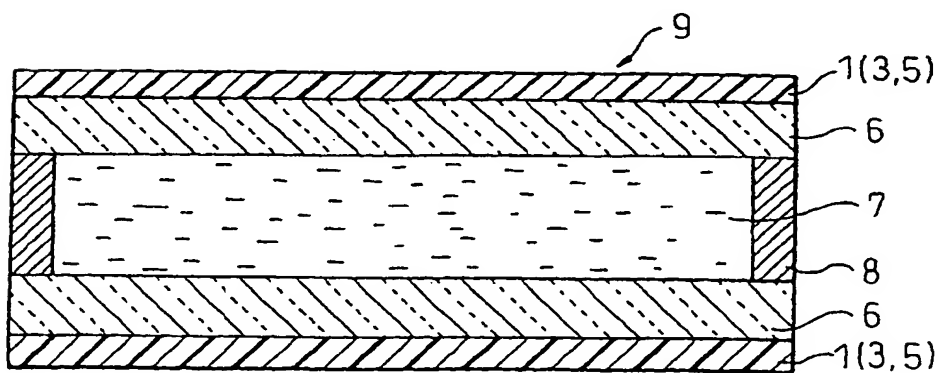


Fig.4



BEST AVAILABLE COPY

Fig. 7

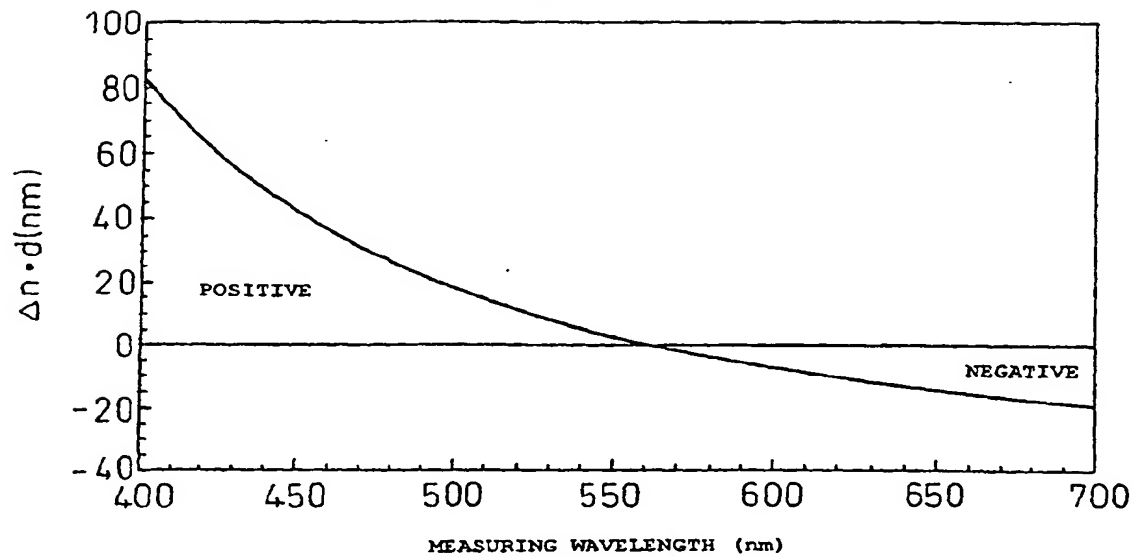
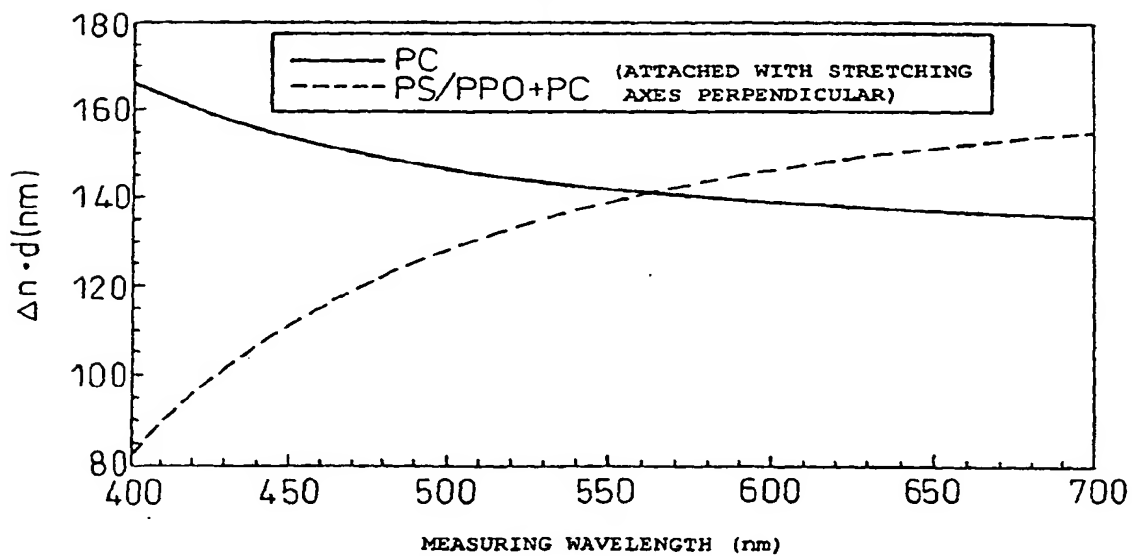


Fig. 8



BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/05118

A. CLASSIFICATION OF SUBJECT MATTER		
Int.Cl. ⁷ G02B5/30, C08G64/06, G02F1/13363, C08J5/18, C08L25/04 //(C08L25/04, C08L71:12), C08L69:00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int.Cl. ⁷ G02B5/30, C08G64/06, G02F1/13363, C08J5/18, C08L25/04 //(C08L25/04, C08L71:12), C08L69:00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 9-297218, A (Sumitomo Chemical Company, Limited), 18 November, 1997 (18.11.97), Full text; all drawings	1-3, 6-15
A	Full text; all drawings (Family: none)	4, 5
Y	JP, 9-297216, A (Sumitomo Chemical Company, Limited), 18 November, 1997 (18.11.97), Full text; all drawings	1-3, 6-15
A	Full text; all drawings (Family: none)	4, 5
A	EP, 554130, A1 (SHARP KK), 04 August, 1993 (04.08.93), Full text; all drawings & JP, 5-210084, A Full text; all drawings & US, 5493431, A & TW, 210388, A	1-15
A	JP, 8-160222, A (Teijin Limited), 21 June, 1996 (21.06.96), Full text; all drawings (Family: none)	4, 5
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 05 September, 2000 (05.09.00)		Date of mailing of the international search report 12 September, 2000 (12.09.00)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)